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Electroactive Block Copolymer Brushes on Multiwalled Carbon Nanotubes

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Electroactive polymers (EAPs) are of interest for present and emerging applications[1] in energy storage devices,[2] electrochromic devices,[3] sensors,[4] and artificial muscles.[5] In these electrochemical devices, EAPs are switched between conductive/colored states by reversible doping and dedoping which requires the diffusion of mobile ions, and therefore high-performance EAP materials should simultaneously have efficient electron conduction and ion transport. The combination of excellent electrical and mechanical properties of carbon nanotubes (CNTs)[6,7] makes them promising candidate materials for a wide range of technological applications.[8] However, the challenge of dispersing these materials, due to their high aspect ratios and strong van der Waals interactions, has been an impediment to many applications. Considerable efforts have been devoted to the covalent functionalization of nanotubes to improve dispersions and to enhance their compatibility in composite materials.[9] Our group has continuing interests in the development of functional polymer/CNT hybrid materials using nanotube covalent functionalization.[10] In this contribution, we report the synthesis of multiwalled CNTs (MWCNTs) adorned with EAP brushes initiating ring-opening metathesis polymerization[11] from the nanotube side walls.[12] In these systems, the nanotube cores serve as the dominant electrical conductors. This feature allows flexibility in the choice of the EPA shells because high bulk conductivities of the polymer component are not necessary for good electroactivity as long as a percolative network of MWCNTs is present. In addition, we designed and synthesized electroactive block copolymer brushes with a shell of ion-conducting polymers surrounding the EAP layer to enhance counterion diffusion.

The synthetic routes to surface-initiated electroactive block copolymer brushes (**5a**) on the MWCNTs are shown in Scheme 1. Norbornene-functionalized MWCNTs, **1a**, were prepared by a reaction sequence initiated by a zwitterionic complex formed by reaction of dimethyl acetylenedicarboxylate and 4-(dimethylamino)pyridine, wherein 5-norbornene-2-methanol was used as the second nucleophile that traps the cationic intermediate.[10] Characterization of **1a** was limited to infrared (IR) spectroscopy due to their poor solubility in organic solvents. The IR spectrum of **1a** (Figure S3)[13] shows absorption signals at 2949, 1653, and 985 cm^{-1}, indicating the incorporation of norbornene groups. Furthermore, the signals at 1720, 1240, and 985 cm^{-1}, corresponding to carbonyl and vinyl ether groups, are consistent with the structure of **1a**. The density of introduced norbornene groups was confirmed by thermogravimetric analysis (TGA), showing a weight loss of 28% at 700 °C compared to pristine nanotubes (Figure 1a). This weight loss corresponds to one functional group for ~50 carbons.

Electroactive norbornene monomer, **2**, with pendant *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) groups was synthesized by a nucleophilic substitution reaction between 5-norbornene-2,3-*endo*-dimethanol with 6-bromohexyl-TMPD (Scheme S1). TMPDs are known to undergo two well-separated chemically and electrochemically reversible one-electron oxidations.[14] Ion-conducting monomer, **3**, with pendant triethyleneoxy methyl ether groups was also synthesized by a similar reaction between norbornene-2,3-*endo*-dimethanol and triethylene glycol monomethyl ether tosylate (Scheme S1). These new compounds were characterized by ^{1}H and ^{13}C NMR and HR-MS.[13] The block polymerization of **2** and **3** was carried out in CH_2Cl_2 using Grubbs second generation Ru catalyst[15] (2 mol % per total monomer **2** + **3**), which is tolerant to a wide variety of functional groups. In the first stage of the polymerization, monomer **2** was quantitatively converted within 3 h, as confirmed by ^{1}H NMR measurements, to produce corresponding poly(**2**) with M_n's of 9400 ($M_w/M_n = 1.77$). Monomer **3** was then added to the mixture, and the resulting mixture was stirred for another 3 h until the complete consumption of **3** was confirmed, leading to well-defined poly(**2**)-*block*-poly(**3**) with M_n's of 13 100 ($M_w/M_n = 2.06$) in high yield. The gel permeation chromatogram revealed a unimodal distribution (Figure S6).[13]

MWCNT-based macroinitiators were prepared by the reaction of norbornene-functionalized nanotubes **1a** with 1 equiv per initiator group of Grubbs second generation Ru catalyst in CH_2Cl_2. Electroactive polymer brush **4a** was synthesized by surface-initiated ring-opening metathesis polymerization (ROMP) of norbornene monomer **2** (25 equiv) in a CH_2Cl_2 suspension of the MWCNT macroinitiators. Monomer **2** was quantitatively converted within 7 h, which was confirmed by a ^{1}H NMR measurement. In addition, block copolymer brush **5a** was synthesized by the subsequent addition of ion-conducting monomer **3** (25 equiv) to the resulting solution of **4a**, and then the resulting mixture was stirred for another 14 h until the complete consumption of **3** was confirmed.

Figure 1b illustrates the dispersibility of pristine nanotubes, functionalized nanotubes **1a**, a mixture of **1a** and poly(**2**), polymer brushes **4a**, and **5a** in CH_2Cl_2. Simple visual indications reveal that poly(**2**)-functionalized nanotubes **4a** display stable dispersions in CH_2Cl_2 after polymerization. Functionalized MWCNTs **1a** do not form stable dispersions in organic solvents even in the presence of poly(**2**). These results provide confirmation of the successful covalent grafting of poly(**2**) from the nanotube surface. Additionally, the excellent dispersibility of **4a** and **5a** allowed for the characterization of the polymerized structure by solution NMR analysis. ^{1}H NMR spectra (Figure S5) of **4a** and **5a** show identical peaks as poly(**2**) and poly(**2**)-*block*-poly(**3**) (Figure S4), respectively.

The content of the grafted polymer chains in the functionalized MWCNTs **4a** and **5a** can be easily detected by TGA measurement, as shown in Figure 1a. The curves of **4a** and **5a** reveal greater weight loss than pristine MWCNTs and **1a**, indicating graft formation. In addition, the weight loss of **4a** and **5a** at 700 °C increases from 95.4 to 98.1 wt % as the feed ratio of **1a** to total amount in the composition falls from 5.1 to 3.0 wt %. Ultrafiltration through a 0.2 μm Teflon filter was employed to remove any polymer that is not covalently attached to the MWCNTs. Although some of the smaller grafted MWCNT materials passed through the membrane, GPC analysis of these materials did not reveal the presence of unbound polymer. Characterization of **4a** and **5a** by transmission electron

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microscopy (TEM) is also consistent with the covalent polymer grafting from the surface of MWCNTs, and Figure 2 clearly reveals nanotubes embedded within a polymer matrix.

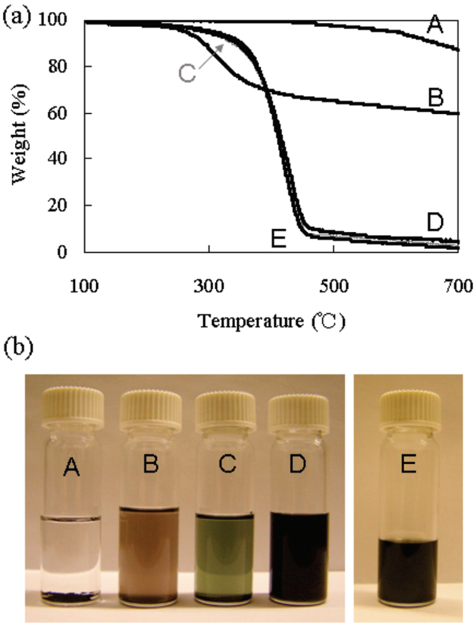


Figure 1. (a) TGA thermograms and (b) photographs illustrating the dispersibility (0.5 mg/mL of nanotubes in CH_2Cl_2, taken 12 h after sonication) of (A) pristine nanotubes, (B) **1a**, (C) a mixture of **1a** and poly(**2**), (D) **4a**, and (E) **5a**.

To better characterize the polymer chains grafted from MWCNTs, we developed another polymer brush **4b** and **5b** that contains ester linkages between nanotubes and EAP by substituting 5-(hydroxyethoxycarbonyl)-2-norbornene in place of 5-norbornene-2-methanol (Scheme S2).[13] Nanotube bound polymer chains could then be cleaved from the MWCNTs by saponification of the ester linkages with KOH/18-crown-6 in THF for 24 h at room temperature.[12a] The MWCNTs were separated from the cleaved polymer by centrifuge as an insoluble black powder, leaving the pure polymer in the solution.[16] GPC analysis of the isolated poly(**2**) and poly(**2**)-*block*-poly(**3**) revealed M_n's of 8600 (M_w/M_n= 2.26) and M_n's of 14 000 (M_w/M_n= 2.31), respectively. The polymers liberated from the MWNCTs displayed similar molecular weights to those from the homogeneously polymerized system (M_n's of 9400, M_w/M_n= 1.77 and M_n's of 13 100 M_w/M_n= 2.06).

The electrochemical behavior of polymer brush films on ITO-coated glass electrodes were studied by cyclic voltammetry (CV) in acetonitrile with n-Bu_4NPF_6 as a supporting electrolyte. Figure 3 shows the CV results of homopoly(**2**), poly(**2**)-*block*-poly(**3**),

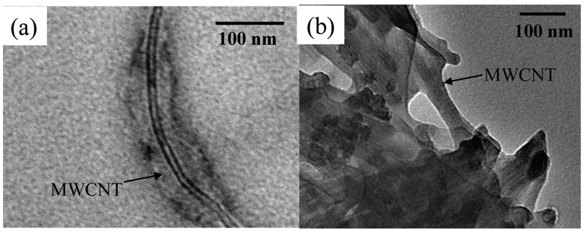
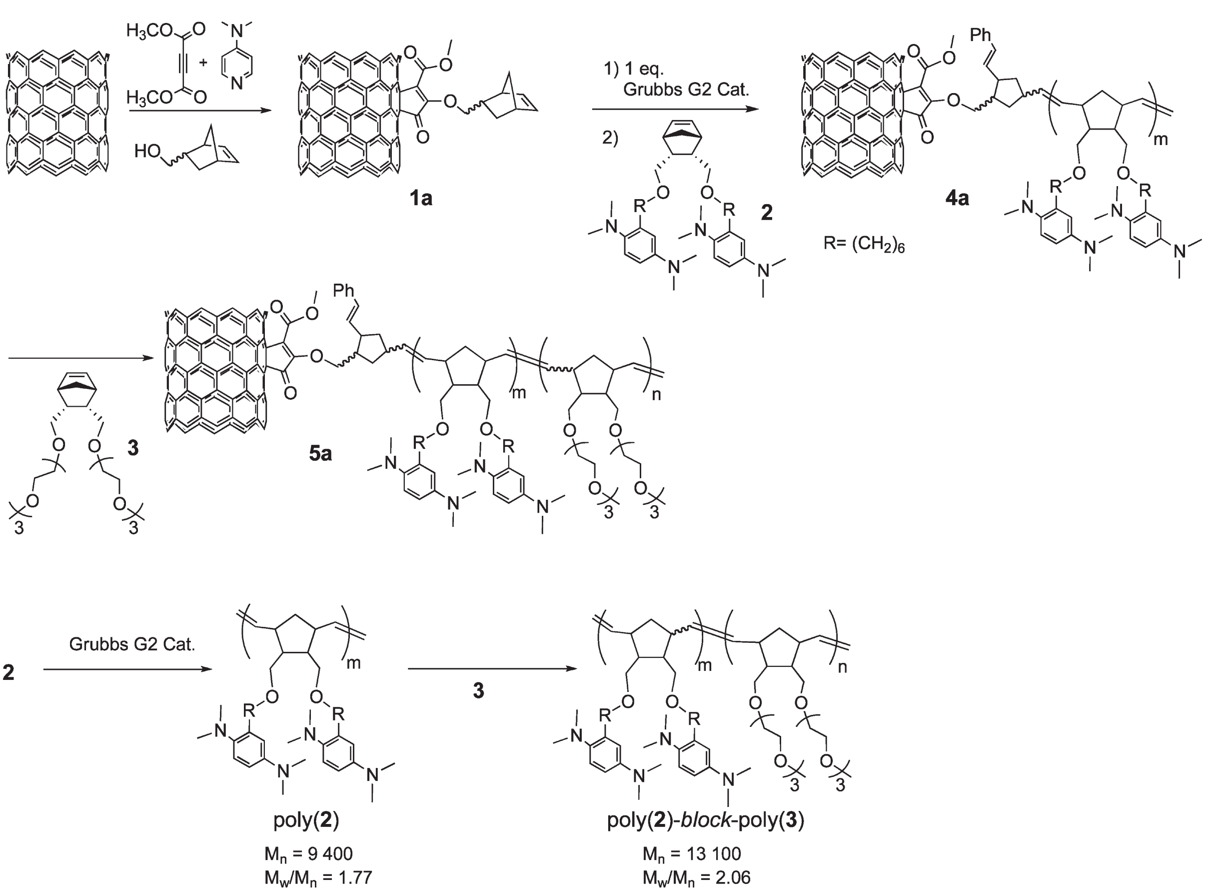


Figure 2. TEM images of (a) polymer brush **4a** and (b) **5a**.

Scheme 1. Syntheses of Norbornene-Functionalized MWCNT (1a), Electroactive Polymer Brush (4a), Block Copolymer Brush (5a), Poly(2), and Poly(2)-*block*-Poly(3)



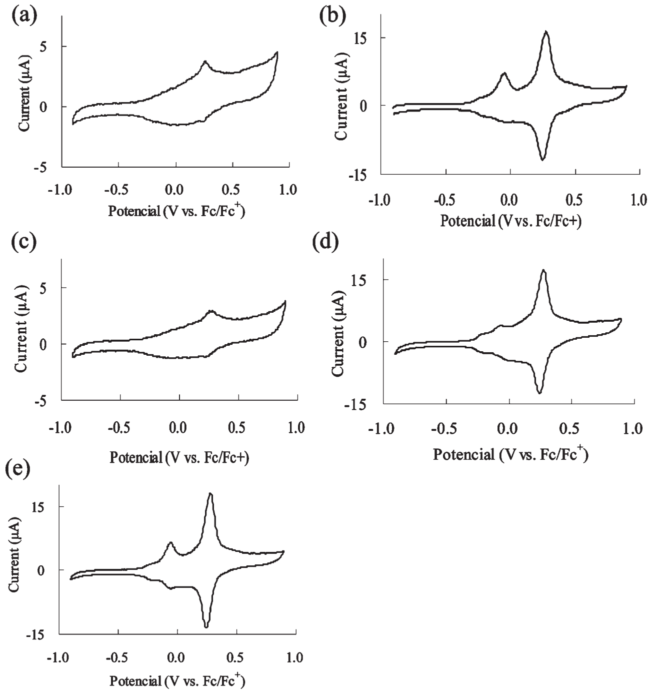


Figure 3. CVs of (a) poly(**2**), (b) poly(**2**)-*block*-poly(**3**), (c) a mixture of **1a** and poly(**2**), (d) functionalized nanotubes **4a**, and (e) **5a** on ITO-coated glass electrodes (electrode area: 49 mm^2). All measurements were carried out on spin-coated films (thickness 40 nm) in CH_3CN with 0.1 M n-Bu_4NPF_6 as a supporting electrolyte, at the scan rate 100 mV s^{-1}.

a mixture of **1a** and poly(**2**), electroactive homopolymer brush **4a**, and block copolymer brush **5a**. To endure similar coverage, we used the same concentrations, volumes, and conditions to spin-cast thin films on ITO. The film thickness of all samples were found to be ~40 nm using a surface profiler. Homopoly(**2**) and the mixture of **1a** and poly(**2**) displayed noticeably lower definition to its CV and ~80% lower electroactivity (based on the TMPD groups, as compared to **5a**). Well-resolved oxidation/reduction peaks for the TMPD molecules were observed for poly(**2**)-*block*-poly(**3**), **4a**, and **5a.** These results indicate that the nanotube cores facilitate electrochemical kinetics (charge diffusion) in the absence of the ion-conducting block. The rapid electrochemical kinetics of the TMPD group are realized in MWCNT-free materials in the presence of the ion-conducting block.

The electrical conductivities of oxidized electroactive homopolymer brush **4a** and block copolymer brush **5a** on cast films were measured by a four-point probe (doping by saturation with iodine vapor). For reference we also measured films formed by casting dispersions of MWCNTs and the MWCNT macroinitiator **1a**, and these materials displayed respective conductivities of 2 and 0.7 S/cm. Although the mixture of **1a** and poly(**2**) was insulating as well as homopoly(**2**) and poly(**2**)-*block*-poly(**3**), both oxidized forms of **4a** and **5a** demonstrated measurable conductivities (ca. 3×10^{-6} S/cm). The conductivities appeared to depend on the content of MWCNTs, and lower molecular weights of grafted polymer of structure **4a** that contained 10 wt % MWCNT exhibited a slightly higher conductivity of 2×10^{-5} S/cm.

In conclusion, we have demonstrated the syntheses of electroactive polymer brushes with MWCNT backbones by grafting nonconjugated polymers containing pendant electroactive groups from the side walls of nanotubes via the surface-initiated ring-opening metathesis polymerization. In addition, we have synthesized block copolymer brushes with a shell of ion-conducting polymers surrounding the EAP. These resultant electroactive materials exhibited high dispersibility in organic solvents and improved electroactivities and conductance in comparison with the homo- and copolymers that were not attached to MWCNTs. The synthetic strategy reported herein can be utilized to prepare a new class of functionalized polymer/carbon nanotubes hybrid materials.

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Supporting Information Available: Experimental details and characterization of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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